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Docket No.: M4065.0505/P505
(PATENT)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of:
Kristy A. Campbell, et al.

Application No.: 10/075,390

Group Art Unit: 2818

Filed: February 15, 2002

Examiner: Not Yet Assigned

For: METHOD TO ALTER
CHALCOGENIDE GLASS FOR
IMPROVED SWITCHING
CHARACTERISTICS

SUBMISSION OF DECLARATION OF TERRY L. GILTON

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

Pursuant to 37 CFR 1.56, the attention of the Patent and Trademark Office is hereby directed to the attached declaration of Terry L. Gilton reporting information which may be deemed material to prosecution.

Dated: September 3, 2003

Respectfully submitted,

By 

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For: METHOD TO ALTER CHALCOGENIDE
GLASS FOR IMPROVED SWITCHING
CHARACTERISTICS

**DECLARATION OF TERRY L. GILTON CALLING ATTENTION TO
INFORMATION PURSUANT TO 37 C.F.R. § 1.56**

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

I, Dr. Terry L. Gilton, do hereby declare and state as follows:

1. I reside at 3149 E. Nature Drive, Boise, Idaho 83706.
2. I am one of the inventors of the invention described and claimed in the above-captioned application.
3. Micron Technology, Inc. ("Micron") is the assignee of the invention claimed in the application identified above.
4. I am employed at Micron as a project manager in charge of supervising a project team in the research and development of new memory devices, specifically including memory devices based on chalcogenide materials. I have held this position since April 2000.

5. The captioned application describes and claims a method to alter chalcogenide glass for improved switching characteristics. The described and claimed invention includes techniques for making a doped chalcogenide glass more rigid by changing the stoichiometry of the chalcogenide glass by, for example, processing the glass in an atmosphere (e.g., oxygen) which results in a stoichiometry change.

6. I am making this Declaration in order to bring to the attention of the U.S. Patent and Trademark Office certain information, which may or may not be deemed material to the prosecution of this application.

7. To my best information and belief, on March 22, 2000, Micron entered into a Research and License Agreement (hereinafter "the Agreement") with Axon Technologies Corp. (hereinafter "Axon") and Michael Kozicki (hereinafter "Kozicki") pursuant to which Axon and/or Kozicki would perform certain research on behalf of and provide information to Micron with respect to Programmable Metallization Cell Technology (hereinafter "PMC" technology).

8. To my best information and belief, pursuant to the Agreement, any requirement of Micron to keep information received from Axon and/or Kozicki confidential has now expired.

9. On May 24, 2000, Kozicki sent an e-mail communication to me including his thoughts regarding adhesion of chalcogenide glass to a substrate during chemical mechanical polishing. He suggested a "low temperature anneal of the glass after deposition (say 200 deg. C)." The communication is attached as Exhibit 1.

10. On May 25, 2000, Kozicki sent an e-mail communication to me relating to, among other things, annealing silver and germanium selenide containing memory devices to stabilize, anneal out stress or densify the glass. The communication is attached as Exhibit 2.

11. On July 5, 2000, Kozicki sent an e-mail communication to me relating to his "torturing" of germanium selenide containing memory devices by heating. The communication is attached as Exhibit 3.

12. On July 28, 2000, Kozicki sent an e-mail communication to me relating to the operational characteristics of germanium selenide containing memory devices at elevated temperatures. The communication is attached as Exhibit 4.

13. On February 20, 2001, Kozicki sent an e-mail communication to me relating to the functioning of germanium selenide containing memory devices at elevated operating temperatures. The communication is attached as Exhibit 5.


14. To the best of my knowledge and belief, the information in Exhibits 1-5 was not disclosed in any publication or otherwise publicly disclosed prior to the respective dates said information was delivered to Micron.

15. I believe the information disclosed in the attached Exhibits does not teach or suggest the subject matter claimed in the above identified application, namely because the application discloses and claims an annealing process conducted in an atmosphere conducive to removing a portion of selenium from a germanium selenide glass which thereby increases the rigidity of the glass layer. While I do not believe any of the Kozicki work reported above was for the purpose of forming a more rigid glass backbone, or was performed in an atmosphere which would produce a more rigid glass backbone, nonetheless, the information is being submitted so the Examiner may draw his/her own conclusions on whether this information is deemed "material" pursuant to 37 C.F.R. § 1.56. The disclosure of this information is not intended as an admission that it is material or that it constitutes prior art with respect to the invention claimed in the above-captioned application.

16. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information or belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of this declaration, the present application, or any patent resulting therefrom.

Further the Declarant Sayeth Not

8/27/03
Date



Terry L. Gilton, Ph.D.

tawilliams

From: Michael Kozicki [michael.kozicki@asu.edu]
Sent: Wednesday, May 24, 2000 3:03 PM
To: 'tgilton'
Subject: RE: Samples
Sensitivity: Confidential

Hello Terry:

Here are my words of pseudo-wisdom on the CMP adhesion problem ...

1. Try a thin layer of CVD SiO₂ on the surface of the nitride - in our limited experience, the glass sticks a little better to SiO₂ than Si₃N₄.
2. Since you have found that the glass sticks to TiN (much to my astonishment!), would this be a good choice of adhesion layer (and left as a barrier material on the dielectric afterwards)?
3. Maria favors a few hundred Angstroms of Cr as an adhesion layer!
4. How about a low temperature anneal of the glass after deposition (say 200 deg. C)? This will definitely make it stick better.

Good luck!

Michael.

Michael N. Kozicki, Ph.D., C.Eng.
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tawilliams

From: tgilton
Sent: Thursday, May 25, 2000 12:12 PM
To: 'Michael Kozicki'; tgilton; Maria Mitkova
Cc: johnmoore
Subject: RE: Samples
Sensitivity: Confidential

Michael,

1. I am using 404.5nm light for the silver exposure and this seems to be just fine. I am exposing a whole wafer at one time in a nifty apparatus that we built. The source is a 1kW mercury lamp with an IR filter and the 404.5nm filter. Currently, I am exposing the wafers for 20 minutes, but I expect that I might be able to go shorter when I get a change to characterize it. I have no idea what the efficiency of the optical system is.

2. We have already annealed 3 wafers (1 W electrode, 1 TiN electrode, and 1 blanket Ge₃Se₇ on Nitride) at 200C in N₂ at 10 Torr. There were no outward changes in the material. They are being polished along with the rest of the lot and we hope to have some devices from them.

As usual, more to come.

Best regards,

Terry G.

-----Original Message-----

From: Michael Kozicki [mailto:michael.kozicki@asu.edu]
Sent: Thursday, May 25, 2000 9:27 AM
To: 'tgilton'; Maria Mitkova
Cc: johnmoore
Subject: RE: Samples
Sensitivity: Confidential

Hello Terry:

Thanks for the cross-section - it looks very impressive (you guys are good)! I'm highly relieved that the adhesion to W is good (it helps to confirm that I'm not going mad after all).

As far as the vacuum break thing is concerned, it has been known for a long time that exposure of chalcogenide glasses to the lab ambient modifies the surface (Maria will send some references to you later today). The nature of the exposed surface is not well understood but we know that something changes as the ambient exposed glass generally exhibits an "incubation period" during silver photodissolution. What this means is that the silver dissolution is greatly slowed down in the first few minutes of exposure but then it jumps to a more normal rate - it's almost as if the changed surface acts as a diffusion barrier which has to be broken down before the silver can get into the glass film. Note that this does not completely prevent silver dissolution, nor does it reduce the amount of silver that can be dissolved in the films, it just slows down the diffusion during the initial period. In the case of Ge₃Se₇, it is reasonable to assume that germanium oxide has something to do with the incubation effect but we were somewhat confused as to how this would form (Ge-Se compounds are very stable at room temperature). Our brainstorming led to the (reasonable) idea that absorption of ambient light of shorter wavelengths would produce defects in the surface region and then you get a defect-enhanced oxidation. It might not be this simple but it is a good working hypothesis. (Final note: When Lyndee did her photodissolution study, she saw a strong incubation effect in arsenic sulfide but it was not nearly as obvious in germanium selenide. This may have been a sample preparation effect or it may be real due to the stability of the latter material.)



I've been thinking a little more about your CMP adhesion problem. I think the best approach is to use the low temperature anneal in a neutral ambient. When we were working with "horizontal" devices involving $\text{Ag}_4\text{As}_2\text{S}_3$, the adhesion of the glass was vastly improved by a half-hour anneal in nitrogen at 130 deg. C. For the case of Ge_3Se_7 , you could almost certainly go much higher (perhaps up to 250 deg. C) as T_g is a lot better. I talked with Maria about this and she thinks that this anneal would be a good idea in any case to "stabilize" the glass (anneal out stress, densify, etc.). Is this a good option for you?

All the best,
Michael.

Michael N. Kozicki, Ph.D., C.Eng.
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<http://ceaspub.eas.asu.edu/csscr/>

-----Original Message-----

From: tgilton [mailto:tgilton@micron.com]
Sent: Thursday, May 25, 2000 6:54 AM
To: 'Maria Mitkova'
Cc: Michael Kozicki; tgilton; johnmoore
Subject: RE: Samples

Thanks Maria, this is interesting. Now I have some more questions:

1. Precisely what do you observe with a vacuum break before silver deposition? I had no problems getting the silver into the Ge_3Se_7 with a long vacuum break. Is there an effect on the amount or state of the silver that might be dissolved into the glass?

2. Can you tell me more about the photo-induced surface defects, or provide a reference? Since we are talking about films as thin as 100Å, the surface is likely to be pretty important.

And now a comment:

The Ge_3Se_7 DOES adhere much better to the W than the TiN! Our EDS analysis in the contact was suspect, so we cross sectioned a wafer, and lo, the activ holes were filled. I have attached one of the cross sections to this.



tawilliams

From: Michael Kozicki [michael.kozicki@asu.edu]
Sent: Wednesday, July 05, 2000 11:16 AM
To: 'rlee'; tgilton
Cc: mdurcan; denniskeller
Subject: RE: Hot devices!
Sensitivity: Confidential

Hello Roger and Terry:

I definitely think it would be a good idea for someone to come down here to see first-hand how we test our devices. Unfortunately, I'm leaving for the UK in a few hours and will not be back until next week (you can reach me at 011-44-797-030-3880). I've made some additional suggestions to Dennis regarding testing so maybe he should try these out first in any case. Perhaps we should reserve Thursday or Friday of next week for ASU testing, if that works for your people (as an added benefit, golf is really cheap this time of year). I have a meeting of campus on Friday afternoon but it will only take me away for a couple of hours.

We have seen some very promising results in the past couple of weeks and are getting a good handle on the role germanium oxide plays. We believe the stuff is getting onto our samples from the germanium selenide source material (the oxide definitely forms on the surface of the chunks during storage) even when we pre-evaporate onto the shutter. Uncontrolled germanium oxide on the cathode can give you an "unstable write" in some devices unless you hammer the electrodeposit through it using multiple writing pulses. When we suspect an oxide is present (a high write threshold is a good clue) we write until we get an on IV characteristic which is linear and which has a resistance which is no higher than 0.18/(programming current in amps). I guarantee that such an on state will be stable at 85 C as long as the solid solution is saturated. The bad news is that this oxide layer is probably also retaining silver during cycling. This retained silver is oxidizable and will cause the devices to write in the reverse direction, resulting in poor cycling characteristics. In general, the plating/contamination of the cathode with silver is a big concern to me.

Which brings me to another point. We have been torturing devices on our hot chuck in the probe station and the results have been very interesting, to say the least. Temperatures above 150 C have a profound effect on devices which have only seen 85 C during processing. Silver seems to be diffusing in from the anode as the off resistance drops dramatically in the heated devices. However, we can reverse this effect electrically by plating the silver back onto where it came from! If we do this at over 150 C, it redissolves within a few seconds. However, if we cool the sample down to 85 C and bias the device at around -0.5 V for a few seconds, the excess silver seems to be removed as the device starts behaving much as it did prior to heating! This suggests that it is indeed a silver migration problem and not some temperature-induced phase separation (the latter could not be reversed electrically). We're running more samples this week to confirm this phenomenon and to determine the effect of temperatures over 85 C during processing (our first experiment in which we gave the device a 100 C anneal following photodiffusion gave us results which were surprisingly good so we are re-running this to determine what happened).

By the way, we have also had devices cycling at 200 C (promising)!

I'll check my e-mail at the weekend so let me know your thoughts and plans.

All the best,
Michael.

Michael N. Kozicki, Ph.D., C.Eng.
Director, Center for Solid State Electronics Research
Professor, Department of Electrical Engineering
Arizona State University
Tempe, AZ 85287-6206

4/23/02



tawilliams

From: Michael Kozicki [michael.kozicki@asu.edu]
S nt: Friday, July 28, 2000 12:03 PM
To: 'rearl'; rlee; denniskeller; tgilton
Cc: mdurcan; Min Yun; Maria Mitkova; Janmichael Aberouette
Subject: CONFIDENTIAL - Thermal effects

Gentlemen:

We have some interesting results on the high temperature operation of our (ASU made) complete devices that I would like to share with you. The devices underwent a 100 C anneal in nitrogen immediately following uv exposure but prior to lift-off of the ternary. We tested them on our probe station with a hot chuck, allowing the devices to stabilize at the stated temperature for ten minutes prior to programming at 10 uA. The devices worked well at room temperature, programming from several Mohms to a very stable 18Mohms.

Operating at:

125 C - a small percentage of unprogrammed devices exhibited a low resistance but this could be easily "erased" to several Mohms and the devices behaved normally after that. Programmed Ron was around 700 ohms.

150 C - many (less than half) of the new devices were in the low resistance state but could be erased and cycled. Programmed Ron was around 600 ohms.

175 C - most of the devices were in the low resistance state to begin with but easily erased to the Mohm range. Programmed Ron was around 150 ohms.

200 C - all of the devices were in the low resistance state to begin with but easily erased to the Mohm range. Programmed Ron was around 100 ohms.

Needless to say, when we cooled the wafer to 85 C after being at 200 C, all devices were in the low resistance state but could be erased/cycled (Ron was about 1 kohm for 10 uA). There was a definite impression that the erase happened more easily at higher temperature due to the higher ion mobility (see later).

There are a couple of interesting points we can take from these results:

1. Thermal processing of finished devices does seem to allow silver to creep down the interface or perhaps through defects/voids in the material to form a low resistance link prior to any programming and this effect gets worse at higher temperature. We also know from our previous experiments at 225 C that this effect also seems to get worse with time, eventually (e.g., after an hour) leading to a connection which apparently is not so easy to erase (however, as I mentioned before, this may be influenced by the domed material in our vias). However, for relatively low temperature operation (125 C or less), it appears that we can always erase this "thermally created" state.

2. For a set programming current limit, the programmed on resistance of the devices gets lower with temperature. The activation energy of this process appears to be around 0.35 eV. This is significant as we believe the activation energy for ion conduction in these highly doped (> 30 at. % Ag) materials is around 0.35 eV. (Note that for less heavily doped material, we think that the activation energy rises to above 0.5 eV.) Although we do not have good data for the off resistance due to noise, this too seemed to trend down with increasing temperature, again due to the higher ion mobility.

Dr. Yun did a split with pre and post lift-off thermal exposure and the early results seem to suggest that the thermal treatment after lift-off leads to a bigger "shorting" problem than heating the film when it is still relatively continuous. In other words, the experiment seems to confirm that silver diffusion in the interface between the chalcogenide and the dielectric does occur during thermal processing. We will do more work on this.

4/23/02



tawilliams

From: Michael Kozicki [michael.kozicki@asu.edu]
Sent: Tuesday, February 20, 2001 8:55 AM
To: 'Terry Gilton'; 'Kris Campbell'
Subject: Tg of 20/80 material

Good morning Terry and Kris:

Forgive me for being somewhat distracted during our meeting - I had too many plates spinning yesterday afternoon and my small brain couldn't handle it! However, I was actually correct about the glass transition temperature of the Ge₂₀Se₈₀ material. Whereas Tg drops with Ag concentration for all the less Se-rich materials, Tg will rise (if only a little) as we add Ag to the 20/80 material. As I understand it (very simplistically), when the Ag reacts with the bridging Se (and chains), it reduces some of the "floppy" modes which give this composition its flexibility and so the structure becomes a bit more rigid. A complicating factor is that many of these materials have two distinct Tgs but I guess we should worry more about the lowest. In any case, I'm pretty certain that Tg for the Ag doped 20/80 stuff will remain above the highest operating temperature of 125 C but is going to be lower than most CVD process temperatures - is this bad or good (frankly, I'm not sure)?

I am definitely most keen on seeing how the new devices stand up to elevated operating temperatures. In the simplest sense, the stability of the electrodeposit depends on how much silver is introduced and retained in the solid solution and on how much "free" (reactable) chalcogen there is. My concern with the more Se rich materials is that even though they are perhaps the most ideal in terms of stability and homogeneity (even after Ag doping), due to the above, they may give us more retention headaches especially if the glasses are "sub-saturated" at the operating temperature. The good news is that we should be able to pump tons of Ag in without any massive phase separation. Any thoughts?

Thanks again for all your hard work and let us know how we can help. I'm going ahead with the material modeling work with Dave Drabold and Otto Sankey (with input from Mike Thorpe) as I feel we really need to do this for device optimization purposes.

All the best,
Michael.

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4/23/02

